III.A.32 Digital Manufacturing of Gradient Meshed SOFC Sealing Composites with Self-Healing Capabilities

Objectives

- Use three-dimensional printing (3DP) technique to build a shape memory alloy (SMA) skeleton for the seal on the seal-interconnect side.
- Use glass to fill the meshed SMA structure and transition into pure glass seal on the electrolyte side.
- Provide gradient coefficient of thermal expansion (CTE) to greatly reduce the thermal stress.
- Further reduce the thermal stresses in the seal by SMA phase transformation toughening.
- Provide self-healing of cracks by SMA shape recovery during SOFC thermal cycling.

Accomplishments

- Fabricated SMA by arc-melting.
- Homogenized and conducted DSC characterization of SMA.
- Developed multiple AutoCAD drawings of wire structure and 3D printed multiple configurations of the wire structure.
- Refined 3DP technique by modifying the print layer thickness, binder solution, and particles sizes used in the 3DP.
- Fabricated glass by mixing reagent grade oxides, high temperature homogenization, and quenching.

Future Work

- Measure the CTE of SMA and glass.
- Examine the glass microstructure.
- Further refine the SMA microstructure and shape memory effort.
- Integrate SMA and glass.

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- Quantify the integrated seal thermal properties and stability.
- Composite seal performance testing.

Introduction

SOFC seals have a demanding set of imposed performance criteria. Of particular importance is the ability to seal between metallic and ceramic components with differing CTEs, and do so while being electrically insulating and exposed to temperature transients from room temperature up to 950ºC. A major roadblock to long-term SOFC operation has been gas leakage through the seal caused by multiple heating and cooling cycles (thermal cycling). The gas seal cracks because the metal and ceramic components that are sealed together shrink and expand differently (CTE mismatch), causing high stresses in the seal.

A host of seal materials has been explored, such as FeCrAlY, DuraFoil, Si-C-N polymers, ceramic and metallic fillers, mica, and glass-ceramic fibers (1-6). However, interdiffusion and durability of some of these materials in the oxidizing environment of SOFC are unknown. Some of these seals require compressive loads or have unknown leakage protection capability. An improved glass matrix should be selected to avoid the above problems. Also, cracking during thermal cycling can be avoided by the integration of a second phase which is a better match to the thermal expansion of the metallic interconnect. A SMA has a CTE close to that of the interconnect and presents the possible benefit of crack healing because of the shape memory behavior when heated.

Approach

The SMA ingot is being fabricated by arc-melting with the desired alloy composition. After the SMA is fabricated, the microstructure and the shape memory effect are characterized. After that, the SMA alloy is broken into small particles and 3D printed into a wire structure. The printed structure is thermally cured and sintered into strengthened wire mesh. Three-dimensional printing allows for the creation of wire diameters between 100-1000 μm and printing layers that are 25-100 μm thick. Sintering densifies the wire mesh and reduces the wire diameter further.

The glass is made by mixing the exact oxide compositions as designed and high temperatures melt the mixture for composition homogenization. The glass melt can be directly infiltrated into the wire mesh to make the final seal or by filling the wire mesh with glass powder and sintering the glass powder and the wire mesh together.

Seal performance testing will be conducted in a bilayer fixture where the top and bottom layers are commercial cell interconnect and electrolyte. The gas composition that passes through the bilayer structure will be varied and samples will be thermally cycled in the bilayer fixture. Seals will be evaluated by microscopy, adherence testing, and residual stress measurements. At the end of each test, interfacial and bulk characterization of the seal will be performed. From these electrochemical, chemical and thermo-mechanical measurements, the overall stability and electrical performance of the seal will be assessed.

Results

The SMA microstructure and the composition have been analyzed by scanning electron microscopy and energy dispersive spectroscopy. The SMA shows dendritic structures, which indicates small composition variation (Figure 1). Based on this, the SMA is being homogenized at 1075°C for 24 hrs and ramped to 1150°C for 48 hrs with the goal of improving its composition homogeneity and shape memory effect. The ingot is being broken down into powder by cold rolling and milling. Cold-rolling strips off the alloy ingot and coldworks the alloy until cracks form and the alloy breaks into ~0.5 cm size pieces. After the alloy is broken into small pieces, it can be milled by ball milling or spex milling to break the pieces into powder. Characterization of the shape memory effect and the CTE are being conducted through DSC and dilatometry, respectively.

Metallic wire meshes have been 3D printed from stainless steel and Ni powders with wire thicknesses of 500 µm and 1 mm, and layer thicknesses of 25 µm – 100 µm. Stainless steel and Ni particles are used to select the optimum printing variables before the SMA is used. Three-dimensional printing with Ni has shown that a binder solution with a higher content of poly-acrylic acid is necessary for Ni based alloys. Figure 2 shows a wire mesh printed from nickel with wire thickness of 500 µm.

Glass material has been fabricated by using >99.9% pure oxides. First, the oxides are milled by a roller mix for homogenization and reducing the size of individual oxide particles. The mixture is then heated in a box furnace for melting and formation of glass. After homogenizing at 1400°C for 2 hrs, the melt is water quenched. A SEM micrograph of the glass material is shown in Figure 3. Currently, the glass microstructure and the CTE are being characterized.

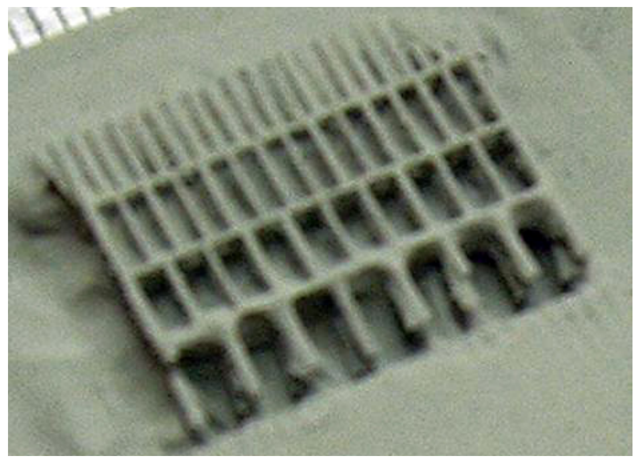

FIGURE 2. 500 μm Wire Diameter Nickel Mesh

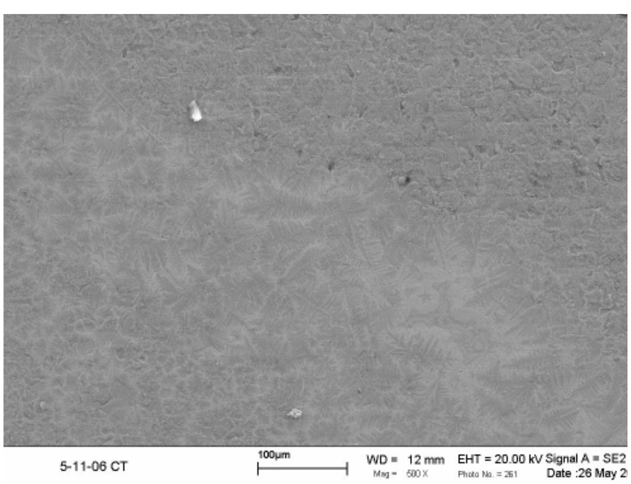

FIGURE 1. SEM Micrograph of the SMA Alloy

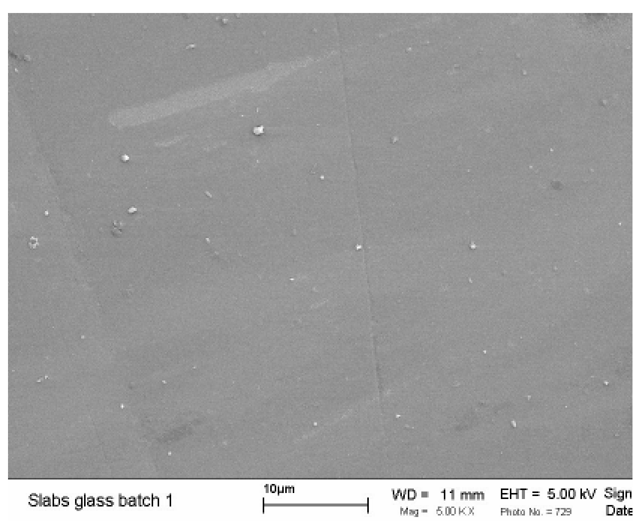

FIGURE 3. SEM Micrograph of the Glass

Conclusions

- SMA has been fabricated by arc-melting.
- SMA has been homogenized by heat treatment. DSC characterization has been conducted.
- AutoCAD drawings of wire structures have been 3D printed.
- Glass has been fabricated by mixing reagent grade oxides, high temperature homogenization, and quenching.

Future Work

- Measure the CTE of SMA and glass.
- Examine the glass microstructure.
- Further refine the SMA microstructure and shape memory effect.
- Integrate SMA and glass.
- Quantify the integrated seal thermal properties and stability.
- Composite seal performance testing.

FY 2006 Publications/Presentations

1. K. Lu, C. Story, and W. T. Reynolds, "Three-Dimensional Printing of Gradient Meshed Solid Oxide Fuel Cell Seal Composites" University Coal Research/Historically Black Colleges and Universities and Other Minority Institutions Contractors Review Conference, June 6-7, 2006. Pittsburgh, PA.

References

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2. K. S. Weil and J. S. Hardy, "Development of a Compliant Seal for Use in Planar Solid Oxide Fuel Cells," *28th International Conference on Advanced Ceramics and Composites*, E. Lara-Curzio and M. J. Readey, eds. 25, pp. 321-326, American Ceramic Society, Cocoa Beach, FL, 2004.

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5. S. Taniguchi, M. Kadowaki, T. Yasuo, Y. Akiyama, Y. Miyake and K. Nishio, "Improvement of Thermal Cycle Characteristics of a Planar-Type Solid Oxide Fuel Cell by Using Ceramic Fiber as Sealing Material," *Journal of Power Sources*, 90, 163–169, 2000.

6. J. W. Fergus, "Sealants for solid oxide fuel cells," Journal of Power Sources, 147, 46-57, 2005.